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- (71) Applicant (*for all designated States except US*): **CRYO-GENESIS AG [CH/CH]**; Hauptstrasse 4, CH-9215 Schoenenberg an der Thur (CH).
- (71) Applicant and
- (72) Inventor (*for US only*): **DAVIS, John, Henry [US/CH]**; Hauptstrasse 4, CH-9215 Schoenenberg (CH).
- (74) Agent: **GILL JENNINGS & EVERY**; Broadgate House, 7 Eldon Street, London EC2M 7LH (GB).
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(54) Title: **EXTRACTION PROCESS**

(57) Abstract: A process for solvent extraction of essential oils from a natural product, in an extraction chamber, comprises introducing pulses of cold solvent. The chamber may be warm relative to the solvent, e.g. butane.

## EXTRACTION PROCESS

### Field of the Invention

This invention relates to an extraction process, and in particular to the solvent-based extraction of essential oils from natural products.

### 5 Background of the Invention

The use of natural products is of increasing commercial interest. Such products, including plants, seeds etc., contain essential oils that can be extracted using a solvent.

The most commonly used solvent for extraction has been carbon dioxide.

- 10 This is usually used in the super-critical phase. This makes it necessary to provide apparatus that can contain high pressures. The expense of carbon dioxide extraction means that it can only typically be used for expensive items or in high volume production, e.g. for pharmaceuticals and instant coffee.

- 15 US-A-5041245 describes the continuous extraction of oil-containing vegetable matter with pressurised, normally gaseous solvent, e.g. propane. This extraction process requires complex apparatus, including a screw feed and compaction of the vegetable matter.

### Summary of the Invention

- 20 The present invention is based on the discovery that solvent extraction is especially effective if conducted using pulses of solvent, and that the resultant extracts are of particularly high quality. In particular, by introducing a pulse or 'slug' of solvent into a relatively warm extraction chamber, more effective extraction is achieved than if there is no difference in temperature. Without wishing to be bound by theory, an explanation for this effect may be that the
- 25 leading edge of the plug goes into the gas phase, giving supercritical extraction, followed by cold solvent extraction.

### Description of the Invention

- The solvent that is used in the invention may be any organic compound that is a solvent for the desired extract. It will usually be a gas under ambient
- 30 conditions. Whereas CO<sub>2</sub> sublimates at -78.5°C (760 mm Hg pressure), a gas used in the present invention may liquefy at a temperature above -60°C and/or below 0°C.

Examples of suitable extractants for use in the invention are hydrocarbon gases such as butane, propane and analogous gases with similar physical properties, or halocarbon variants such as the Freons. The terms "hydrocarbon" and "halocarbon", as used herein, do not exclude halohydrocarbons or indeed  
5 other substituents on carbon.

Hydrocarbons and halocarbons are readily available, and their use does not require that the extraction apparatus should withstand such high pressures as for  $\text{scCO}_2$ . The apparatus can therefore be constructed cheaply and simply. Further, the reduced costs and reduced complexity of the novel method give it  
10 a much wider variety of uses in the preparation of flavourings, nutraceutical extracts, cosmetic extracts etc.

This invention can be used to extract extractant-soluble material from a wide variety of samples. These include plants such as flowers, vegetables, fruit and seeds, and foodstuffs. The sample may be fresh or dried. When plants  
15 from different species are combined in the extraction chamber together to be extracted as one, the oils may undergo a reaction in the chamber, and combined to produce new molecules of a completely new oil. Without wishing to be bound by theory, the new oils may exhibit different crystal formations than either of the original oils, and cannot be separated into the original oils.

20 A suitable operating procedure, and suitable apparatus, will now be described by way of illustration only, with reference to the accompanying drawings. The drawings are an exploded view of an extraction chamber comprising a well casing-type tube 1 having an O-ring 2 at its upper end, above which may be placed a cover 3A or 3B having an compressed air inlet 4 (for the  
25 PSCE variant described below), a gas (extractant) nozzle/venturi inlet 5 and a pressure gauge 6; at its lower end, there are an oil collection chamber 7 having an outlet drain 8 and, separating the chamber from the tube, an O-ring 9 and a filter base plate 10. In addition, there are an inlet 11 and an outlet 12 for water, as part of a warming circuit.

30 The collection chamber should have a valve on it for collecting the gas from the extracts. The chamber should be valved from the extraction pipe as well. If a clear hose can be used between the two, the colour of the liquid gas

can be seen. This is utilised, to determine if extraction is complete. The ends of the pipe may be removed for insertion and removal of spent materials.

In a typical procedure using such apparatus, the sample from which the oil fractions are to be removed is placed in the extraction chamber, which is typically in the form of an upright cylinder, and which is typically made of metal, preferably stainless steel. The extraction chamber may be of almost any dimension, from as small as a few cm<sup>3</sup> in cases where extractions are to be made from rare, precious or test samples, to chambers large enough to contain 1 tonne or more of sample material, for full-scale commercial/industrial applications. Plants have already been built at both these scales, and found to operate equally efficiently in a wide range of ambient temperatures. Further, suitable apparatus may be made portable, e.g. for use in the field to check for the best time for oil harvest from oil plants, seeds, roots, leaves etc.

In some cases, it may be preferable to pack the sample in as tightly as possible, and this can be done by tamping, or by using an air or hydraulic ram or similar technique. It is generally easier to pack the sample material in from the top, pushing it down to the base where it may be retained by a (removable) filter base-plate. This is typically a stainless steel disc with perforations too small to allow the material through, but large enough to permit passage of the oil fraction. Once the sample is in the extraction chamber, the lower oil collection chamber and the top plate are fastened into place, as illustrated in the drawings.

The carrier/solvent gas, e.g. butane, in gaseous or in liquid pressurised form, is pumped or gravity fed into the extraction chamber through the gas inlet, e.g. at a pressure of 0 to 100 bar, preferably 0 to 5 bar. It enters the extraction chamber through a venturi nozzle which is designed to allow a degree of liquid-to-gas transformation, so that significant adiabatic cooling takes place. The cold gas flows down through the column, freezing the sample, and the remaining liquid carrier/solvent more or less simultaneously dissolves out all lipid and lipid-soluble elements ('the oils'). The liquid gas carrier/solvent with its load of dissolved oils flows down to the base of the extraction chamber, where controlled warming is applied, typically with a water circuit.

The wave of cooling which passes down through the extraction chamber may be important, as it can cause freezing of aqueous components in the sample material and thereby prevent them from flowing out together with the oils. This prevents the formation of oil-water mixtures or emulsions which may be unstable, and which may contain substances which could lead to degradation of the oils. The freezing, and the consequent retention of the aqueous phase, also make it possible to extract from fresh source material, with consequent improvements in the profile of the extract. The cooling may also be critical in capturing volatiles and thermo-labile components in the sample material; such components include ketones, esters and aldehydes which might otherwise be lost and/or destroyed in steam distillation or when other solvents are used with higher boiling points, are captured in the oils. This gives the oils a taste and olfactory profile which is unique in capturing the high notes as well as the base notes of the original fresh material.

Controlled warming can be achieved, at the base of the extraction chamber. This may be sufficient to turn much or all of the liquid solvent which has reached the base of the extraction chamber, back into a gas. The resulting expansion builds up pressure inside the extraction chamber, and this pressure can be utilised, to force the oils out through the base, e.g. perforations in a metal filter base plate, and into the lower oil collection chamber. The collection chamber may have a vent near its upper surface, which allows air to be expelled from the collection chamber as the oils enter. If any oil appears at this vent, this is a signal to begin to draw the oils from the collection chamber via the outlet drain in the floor of the collection chamber.

If desired, the oils may be allowed to stand for a short time at room temperature, to allow any remaining traces of dissolved carrier/solvent to evaporate, before being decanted into more permanent storage. If the residue is particularly viscous, a partial vacuum may be used, to accelerate removal of the carrier.

In a variant of this process, the warming circuit is attached to the collection chamber. In this variant, the solvent/carrier liquid and its load of dissolved oils pass out of the extraction chamber into the collection chamber.

Warming and/or a partial vacuum is then applied, causing the gas to evaporate, leaving the oils in the collection chamber.

Timing and pressure inside the extraction chamber should be controlled. Progress of the moving front of cooling and extraction as it passes down the  
5 extraction chamber should ideally be monitored; this can be done most simply (but quite effectively) by observation, and the inflow of liquid gas into the extraction chamber may be stopped when the frost which appears on the external surface of the extraction chamber reaches the bottom.

Depending on the temperature of the column, wavefronts of solvent are  
10 either supercritical fluid or liquid, or some combination of the two. The pulsed variants described are termed pulsed liquid extraction (PLE), pulsed mixed extraction (PME), and pulsed supercritical fluid extraction (PSFE). PLE, PME and PSFE have the twin advantages of using less solvent, which is important in non-enclosed systems (see section below re recycling of solvent); and achieving  
15 a high efficiency of extraction per unit of time.

Pressures and temperatures may need to be controlled and altered, depending on the characteristics of the sample which is being extracted, and on the solvent/carrier being used. The depth, volume and frequency of the solvent slug are also important, and can be chosen by the operator. The optimal  
20 selection of these operating parameters may vary, but may be determined by one skilled in the art, and when properly employed, extraction is effectively total. Samples which have been subjected to a second pass in the extraction chamber typically yield little if any oils.

If desired, the extractant gas is allowed to vent off once the extraction is  
25 complete. In a preferred embodiment of the process, the controlled warming is allowed to progress until all the extractant has gasified, and vented out of the extraction and collection chambers, which can most easily be done via the original gas inlet. As the solvent is drawn off as a gas, it is absolutely pure, and contains no oils from the processed sample. It can then be recompressed for  
30 subsequent re-use.

It will be evident that the entire process acts not only as an oil-extracting system but also as a heat exchanger. In a preferred mode of operation, the

heating and cooling sides of the gas/liquid compression/expansion cycle are used to modify the temperature of the environment where the process is taking place.

Accordingly, the process of the invention may be conducted in what is  
5 effectively a closed circuit, somewhat similar to a refrigeration circuit or heat exchanger. The cooled liquid/gas mix freezes the organic matter, so that unwanted aqueous materials remain *in situ*. The lipid-soluble elements in the sample are dissolved into the remaining liquid carrier/solvent, and flow to the bottom of the expansion chamber. Optionally, the solvent/solute mix is drawn off  
10 into a second collection chamber. In either case, controlled and slight warming is applied directly or indirectly to the solvent/solute mix. This can be just sufficient to achieve the transition temperature of the extractant, so that the liquid evaporates out of the solvent/solute mixture, leaving a residue which consists solely of the oils and other lipid-soluble elements in the organic sample, and  
15 which can be drawn off into a collection vessel. The extractant gas is recovered, generally in the extraction chamber, recompressed, and returned to the original tank for reuse.

If desired, a series of extractions may be adopted, using progressively more polar solvents, in order to elute progressively more polar and hydrophilic  
20 molecules from the original sample. In bench-top experiments and in pilot-scale extraction plants, extraction efficiency rates of close to 100% have been attained.

In addition to obtaining extracts, the novel process has an additional advantage. Once the oils have been removed (from, for example, nuts), the  
25 remainder may be a low-calorie, fat-free nut, having good taste. In a variant of the process, it can also be used as a decontamination procedure. For example, oils can be removed from contaminated materials, i.e. fouled oil filters, or sand or soil contaminated with oil spill or seepage. When these materials are processed, there is a very complete de-oiling. Indeed, oil-contaminated soil may  
30 become fertile once more; and the oils thus removed are generally sufficiently clean to be used for their original purposes.

The following experiments A and B were conducted in order to illustrate the merits of using pulsed extraction.

A. Pass a known volume of solvent (5L) through a standard vegetable sample (5K) in one slug.

5 B. Pass the same volume of solvent through the standard vegetable sample, but in two equal slugs.

Timing of complete extraction may vary, depending on density of packed material in extraction column, but is typically between 5 and 20 minutes. In extreme cases, the extraction time may extend to a few hours. Running  
10 temperatures are typically between  $-5^{\circ}\text{C}$  and  $+5^{\circ}\text{C}$ . The general principle of increased extraction efficiency holds through almost all of the above parametric range.

In the case of crushed garlic, flow rates vary (obviously) depending on the volume of the extraction chamber used. In our example, the column size was  
15 such that the extraction was complete in 10-20 minutes, with flow rates of approx. 1 litre/4 minutes, at a temperature of between  $-2^{\circ}\text{C}$  and  $2^{\circ}\text{C}$ . In the single pulse method (method A), the full 5 litres of solvent was passed through the column, in a time of about 10 minutes. In the pulsed variant (method B), 2.5 litres was passed through in about 5 minutes, and then the second 2.5 litres was  
20 passed through in a similar time. Method B produced an oil volume (1 L) some 33% greater than method A (0.75 L).

If the volume of solvent in each pulse is too low, then each pulse may reach saturation before it can dissolve out sufficient solute, and extraction efficiency declines. However, the general principle (that pulsing is better than  
25 a single pass) remains true unless the volume of solvent used in a single pulse exceeds some threshold value so that it becomes effectively complete extraction. At this point, the advantages of pulsed extraction disappear. However, at this point also the single pass method requires higher volumes of solvent and longer processing times, and is less therefore less cost-effective.

30 In more general terms, the following rule of thumb may apply: Using a defined volume of solvent (e.g., 1000 ml), the most complete extraction of a material (e.g., 100 g) can be made by dividing the solvent into several smaller



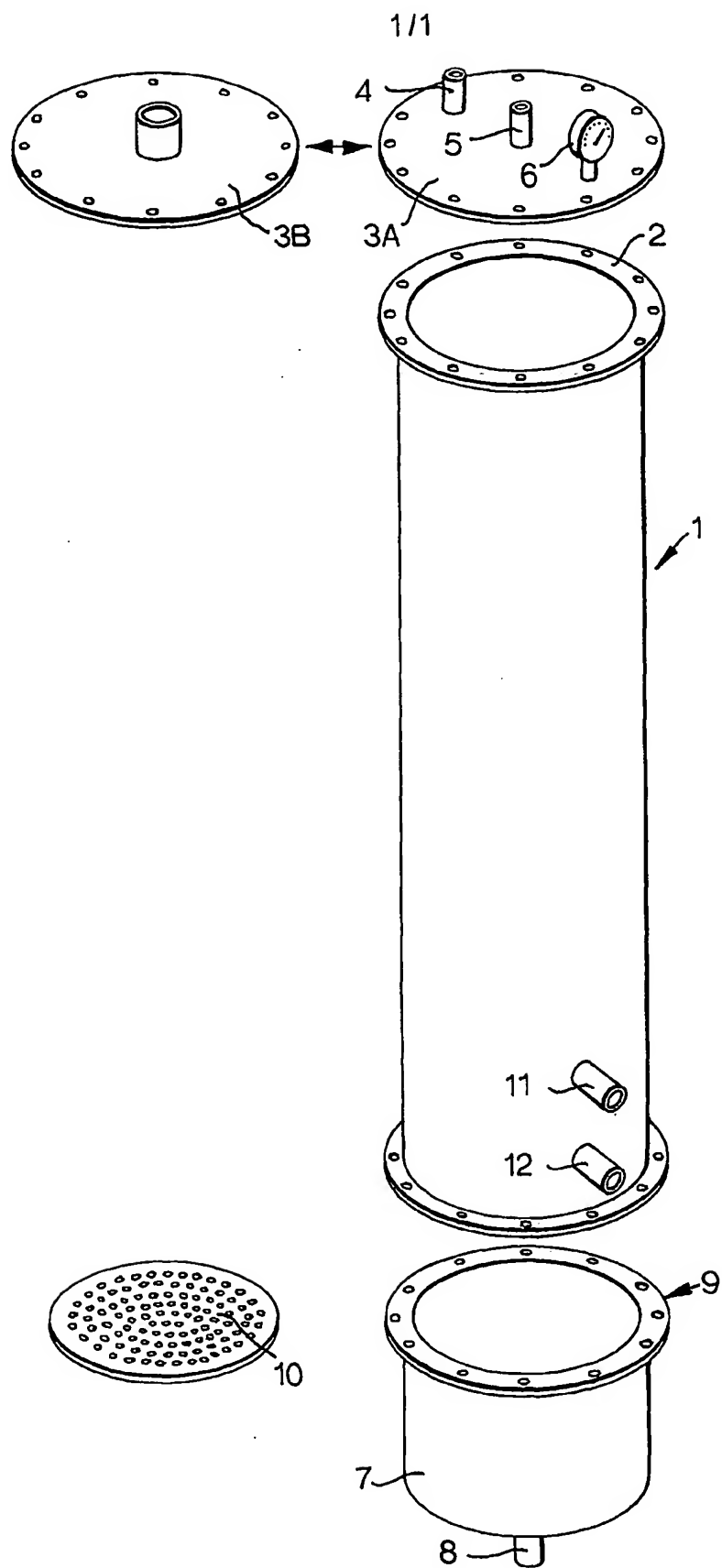
portions (e.g., 5 x 200 ml each) and sequentially extracting, rather than using the entire volume to make one extract of the material. In practice, this means that the carrying capacity of the solvent will be more completely saturated with the first portion of extract and less so in the subsequent extracts. Without wishing to be

5 bound by theory, this phenomenon may be related to the fact that a migration equilibrium of the active agent is established between the solvent and the ballast. The ballast is the source material from which the extraction is being made. Once an equilibrium has been established in a simple pass with a large volume of solvent, no more extraction occurs. Therefore, repeatedly upsetting

10 this equilibrium (more, smaller extractions) starts the process over again each time (with the active agent that remains in the ballast). These subsequent extractions also "wash out" the small amounts of remaining, previous solvent that does not drain from the ballast (although this might also be accomplished by squeezing the ballast).

CLAIMS

1. A process for solvent extraction of oils, in an extraction chamber, which comprises introducing pulses of cold solvent.
2. A process according to claim 1, wherein the solvent has a boiling point of  
5 from -60°C to 0°C.
3. A process according to claim 1 or claim 2, wherein the solvent is a halocarbon or hydrocarbon.
4. A process according to claim 3, wherein the solvent is butane or propane.
5. A process according to any preceding claim, wherein the solvent is  
10 introduced into the chamber as a liquid or gas, and from which the oils can be separated, e.g. under gravity/pressure.
6. A process according to any preceding claim, which comprises separating and recycling the solvent.
7. A process according to any preceding claim, wherein the solvent is  
15 organic and the temperature of the solvent is such that aqueous components remain frozen during extraction.
8. A process according to any preceding claim, wherein the chamber is warm relative to the solvent.
9. A process according to any preceding claim, wherein the oils are  
20 extracted from a natural product.
10. A process according to claim 9, wherein the product is fresh.



Internal Application No. \_\_\_\_\_

PC1/EP 01/08301

### A. CLASSIFICATION OF SUBJECT MATTER

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IPC 7 C11B9/02 C11B1/10

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C11B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X-	US 2 254 245 A (HENRY ROSENTHAL) -- 2 September 1941 (1941-09-02) page 1, line 1 - line 8; claims 1-9 ---	1-10
X	US 5 980 964 A (DODDS JUSTIN ET AL) 9 November 1999 (1999-11-09) column 2, line 21 - column 5, line 2 ---	1-10
P,X	US 6 225 483 B1 (FRANKE HENRY L) 1 May 2001 (2001-05-01) column 7, line 61 - column 10, line 8 ---	1-10
X	US 1 802 533 A (EMMET REID EBENEZER) 28 April 1931 (1931-04-28) page 1, line 5 - line 7 page 2, line 23 - line 98; claims 1-3 ---	1-6,8-10
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☒ Further documents are listed in the continuation of box C.



☒ Patent family members are listed in annex.

\* Special categories of cited documents :

- \*A\* document defining the general state of the art which is not considered to be of particular relevance
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Name and mailing address of the ISA  
European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
Fax: (+31-70) 340-3016

Authorized officer .

Degen, M

## INTERNATIONAL SEARCH REPORT

Inte 1st Application No

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## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 812 903 A (AGRITECH INT LLC) 17 December 1997 (1997-12-17) abstract; claims 1-4 -----	1-6, 8-10

## INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 01/08301

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 2254245	A	02-09-1941	NONE	
US 5980964	A	09-11-1999	NONE	
US 6225483	B1	01-05-2001	NONE	
US 1802533	A	28-04-1931	NONE	
EP 0812903	A	17-12-1997	AU 434606 B	02-04-1973
			JP 9302376 A	25-11-1997
			US 5516923 A	14-05-1996
			EP 0812903 A1	17-12-1997
			AU 5217896 A	13-11-1997
			AU 5217869 A	24-09-1970